# Two caesium vanadium hydrogenphosphates with tunnelled structures: Cs2V2O3(PO4)(HPO4) and Cs2[(VO)3(HPO4)4(H2O)].H2O

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# Two caesium vanadium hydrogenphosphates with tunnelled structures: $Cs_2V_2O_3(PO_4)(HPO_4)$ and $Cs_2[(VO)_3(HPO_4)_4(H_2O)]\cdot H_2O$

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Dicaesium divanadium trioxide phosphate hydrogenphosphate, $Cs_2V_2O_3(PO_4)(HPO_4)$, (I), and dicaesium tris[oxidovanadate(IV)] hydrogenphosphate dihydrate, $Cs_2[(VO)_3(HPO_4)_4(H_2O)]\cdot H_2O$, (II), crystallize in the monoclinic system with all atoms in general positions. The structures of the two compounds are built up from $VO_6$ octahedra and $PO_4$ tetrahedra. In (I), infinite chains of corner-sharing $VO_6$ octahedra are connected to $V_2O_{10}$ dimers by phosphate and hydrogenphosphate groups, while in (II) three vanadium octahedra share vertices leading to $V_3O_{15}(H_2O)$ trimers separated by hydrogenphosphate groups. Both structures show three-dimensional frameworks with tunnels in which $Cs^+$ cations are located.

## Comment

Vanadium phosphates and hydrogenphosphates have been extensively studied because of their interesting properties in catalysis, for example, the oxidation of light hydrocarbons into maleic anhydride, in low-dimensional magnetism and in ion exchange (Boudin *et al.*, 2000). Previous studies involving hydrothermal preparation of vanadium phosphate compounds with insertion of $Cs^+$ cations led to the isolation of several different structural types. The $V^V$ phase $Cs(VO_2)(HPO_4)$ was first isolated (Preuss *et al.*, 1975) and then its structure proposed many years later (Amorós *et al.*, 1988). Subsequently, the $V^{III}$ compounds $CsV(HP_3O_{10})$ (Klinkert *et al.*, 1988) and $Cs[V_2(PO_4)(HPO_4)_2(H_2O)_2]$ (Haushalter *et al.*, 1993), and the mixed-valence $V^{IV}/V^V$ compounds $Cs(V_2O_3)(HPO_4)_2(H_2O)$ (Haushalter *et al.*, 1994) and $Cs_{5.9}(VO)_{10}(PO_4)_4(HPO_4)_8$ (Le Fur *et al.*, 2001) were also isolated. The most interesting remains $Cs_3[V_5O_9(PO_4)_3]\cdot 4.5H_2O$, due to its high degree of porosity which leads to ion-exchange properties (Khan *et al.*, 1996). During our current investigations, the mixed phosphate/hydrogenphosphate $Cs_2V_2O_3(PO_4)(HPO_4)$, (I), and the hydrogenphosphate $Cs_2[(VO)_3(HPO_4)_4(H_2O)]\cdot H_2O$, (II), have been synthesized and their structures solved using single-crystal X-ray diffraction.

The asymmetric unit of (I) contains 17 crystallographically independent non-H atoms: two V atoms with different oxidation states (V1 +4 and V2 +5), two P atoms (P1 and P2) forming phosphate and hydrogenphosphate groups, respectively, and two Cs and 11 O atoms (Fig. 1*a*). The VPO framework consists of $[V2_2^VO_{10}]$ dimers connected through phosphate bridges to $[V1^{IV}O(HPO_4)]$ infinite chains of corner-sharing $VO_6$ octahedra that run along *a* (Fig. 2*a*). This results

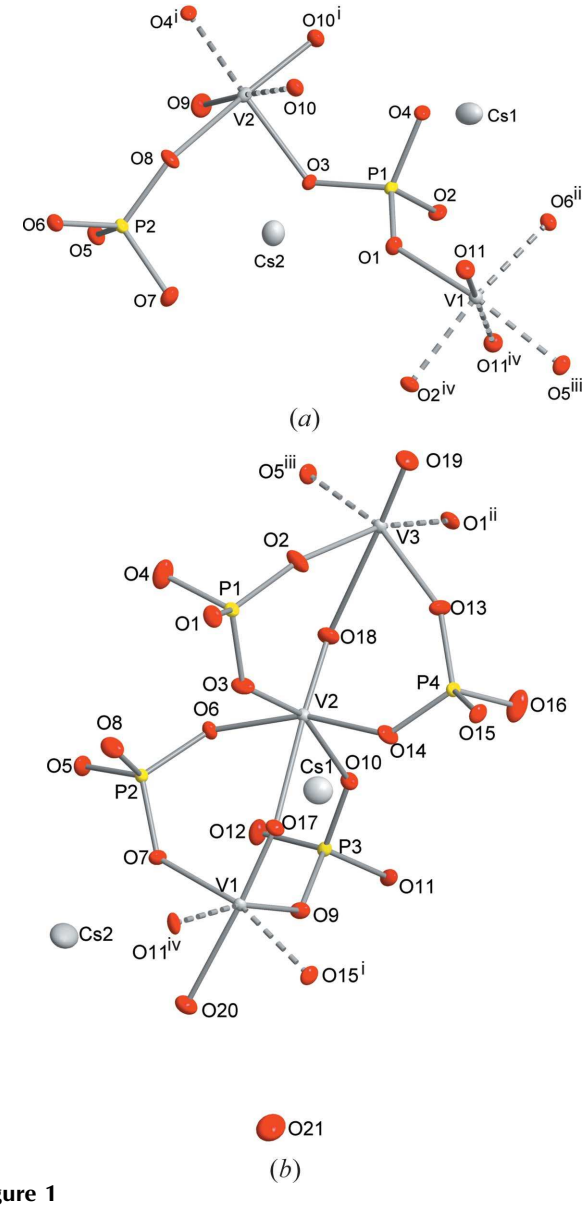


**Figure 1**
The asymmetric unit and vanadium coordination spheres of (*a*) (I) [symmetry codes: (i) $-x, 1-y, -z$; (ii) $1+x, y, z$; (iii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$] and (*b*) (II) [symmetry codes: (i) $-x, -y, -z$; (ii) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $1-x, -y, -z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$]. Displacement ellipsoids are drawn at the 50% probability level.

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in a three-dimensional framework in which tunnels develop along *c* that interconnect tunnels running along *a*. The $Cs^+$ ions lie inside the tunnels (Fig. 2*b*). Within the dimer, the two $VO_6$ octahedra [1.629 (2) Å $\leq d_{V-O} \leq$ 2.339 (2) Å] are connected by edge sharing. In the infinite chains, alternating V=O···V bonds are observed [$d_{V=O}$ = 1.618 (2) Å and $d_{V\cdots O}$ = 2.389 (2) Å], with a V—O—V angle at the shared O1 atom of 129.11 (11)°. The four equatorial O atoms of the octahedra [1.958 (2) Å $\leq d_{V-O} \leq$ 2.002 (2) Å] are shared with phosphate and hydrogenphosphate groups. The phosphate groups share two O atoms with V2 atoms in the dimer and the other two with V1 atoms in the chain. In the hydrogenphosphate groups, two O atoms are shared with the vanadium chain and one with a dimer. The last O atom (O7) is unshared and the P1—O7 distance [1.588 (2) Å] is long enough to suggest the presence of an acidic H atom connected to this O atom. None of the H atoms were located in the structure analysis. The bond-valence-sum calculation gives values of 4.09 and 4.88 for V1 and V2, respectively, indicating formal oxidation states of +4 for V1 and +5 for V2. The structure of (I) can be compared to that of $Cs(V_2O_3)(HPO_4)_2(H_2O)$ described by Haushalter *et al.* (1994). Both structures are built up from infinite chains of corner-sharing vanadium octahedra and present tunnels, running along the infinite chain, occupied by $Cs^+$ cations. In the case of $Cs(V_2O_3)(HPO_4)_2(H_2O)$, the chains are connected directly by hydrogenphosphate groups, generating narrow tunnels, while in (I) the tunnels are larger due to the presence of the $V_2O_{10}$ dimers which act as spacing agents. In both structures, mixed valence is observed. In (I), the tetravalent V atoms are observed in the chains and the pentavalent V atoms in the dimer, while in the case of $Cs(V_2O_3)(HPO_4)_2(H_2O)$ there is an alternation of $V^V$ and $V^{IV}$ within the infinite chain which is evidenced by the quite distinct V···O distances.

The asymmetric unit of (II) contains three crystallographically independent $V^{IV}$ atoms in octahedral environments and four hydrogenphosphate anions (Fig. 1*b*). V1 is coordinated to one terminal oxide O atom, four phosphate O atoms and a water molecule, while V2 and V3 are coordinated to one terminal oxide O atom, four phosphate O atoms and one oxide O atom from an adjacent vanadyl group. The short V=O bonds are in the range 1.592 (2) Å $\leq d_{V=O} \leq$ 1.618 (2) Å and the equatorial distances are in the range 1.959 (2) Å $\leq d_{V=O} \leq$ 2.018 (2) Å, while the long V···O

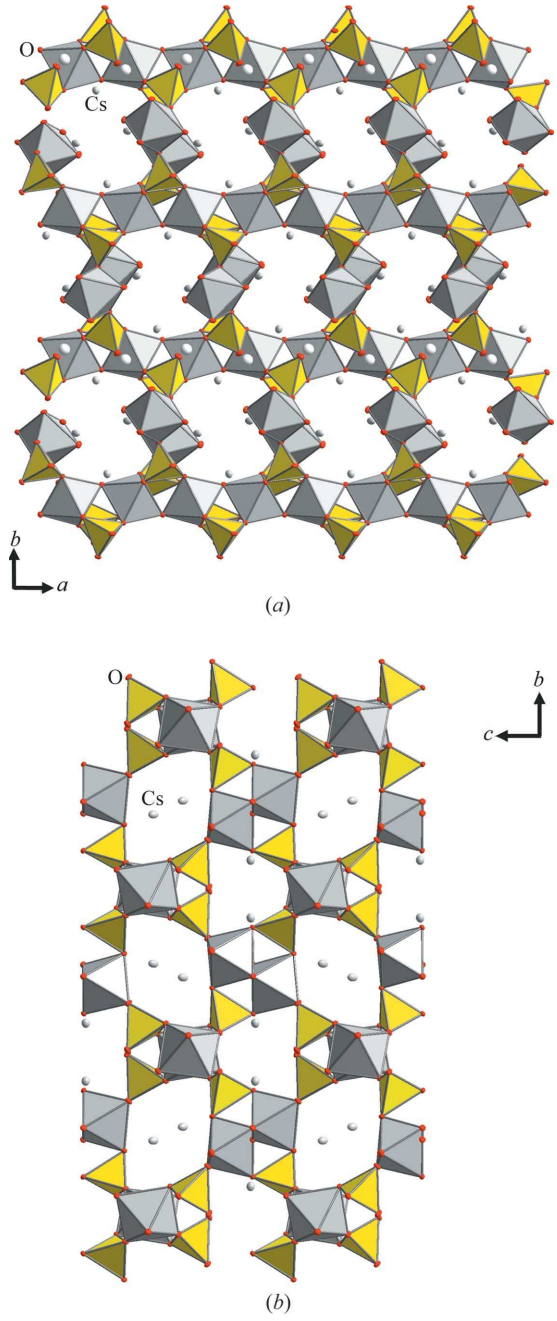


**Figure 2**
Projections along (*a*) the [001] direction and (*b*) the [100] direction of (I), showing the vanadium octahedra (grey in the electronic version of the paper), the phosphate tetrahedra (yellow), the O atoms (red) and the $Cs^+$ cations (white) in the channels.

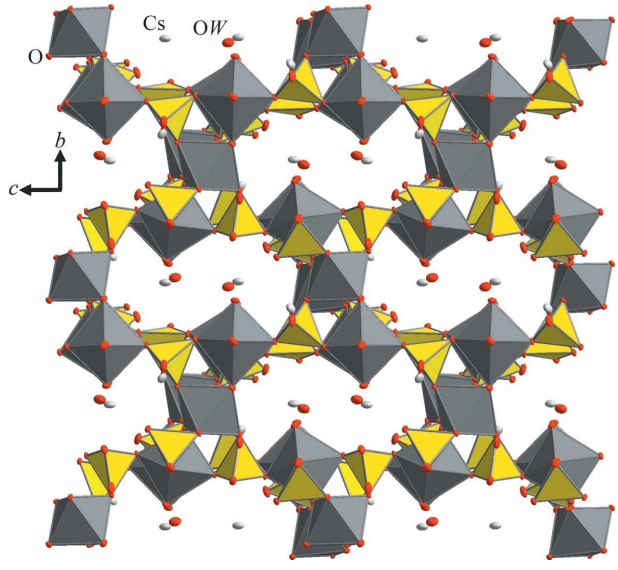


**Figure 3**
Projection along the [100] direction of (II), showing the vanadium octahedra (grey in the electronic version of the paper), the phosphate tetrahedra (yellow), the O atoms (red) and the $Cs^+$ cations (white) in the channels together with water molecules.

distances are in the range 2.244 (2) Å $\leq d_{V\cdots O} \leq$ 2.634 (2) Å. Within the hydrogenphosphate groups, two sets of distances are observed. The first corresponds to O atoms shared with V atoms [1.493 (2) Å $\leq d_{P-O} \leq$ 1.535 (2) Å] and the second to longer P—O distances to unshared O atoms [1.562 (2) Å $\leq d_{P-O} \leq$ 1.599 (2) Å] that are presumed to be protonated. No H atoms could be located in the structure analysis. The three vanadium octahedra share vertices to form a distorted trimer. Each hydrogenphosphate group is linked to two vanadium octahedra of a trimer through $\mu_2$-oxide bridges. One O atom is shared with another trimer and the last one is a terminal OH group. This leads to a three-dimensional framework (Fig. 3) with tunnels running along *a* in which $Cs^+$ cations and water molecules are located. Similar trimers have already been encountered in $H_3N(CH_2)_3NH_3[(VO)_3(OH)_2(H_2O)(PO_4)_2]$ (Soghomonian *et al.*, 1993), in which the trimers are built up from a central square pyramid in which the vanadium shares O atoms from the basal plane with two adjacent V atoms in octahedral coordination. The trimer observed in (II) is actually more similar to that of the phosphite-containing compound $(C_2N_2H_{10})[(VO)_3(H_2O)(HPO_3)_4]\cdot H_2O$ (Zhang *et al.*, 2005), as shown in Fig. 4. The differences between the two structures are in the slightly different tilting of the phosphorus–oxygen groups. This may have its origin in the nature of the counter-cations: quasi-spherical $Cs^+$ in our structure and nonsymmetric propylenediammonium in the phosphite compound.

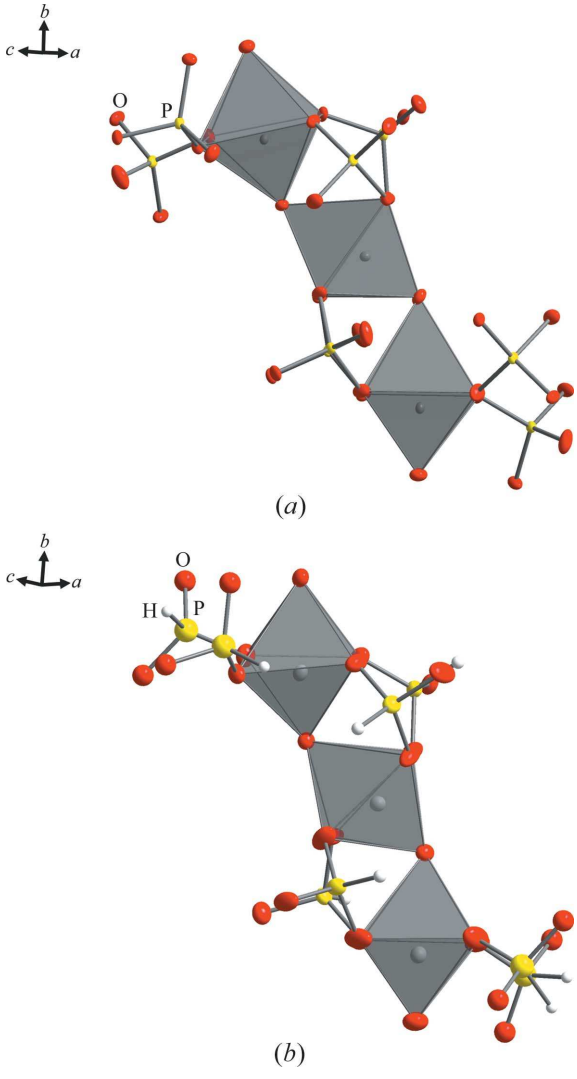


**Figure 4**
Partial views of the trimers in (*a*) (II) and (*b*) $(C_2H_{10}N_2)[(VO)_3(H_2O)(HPO_3)_4]\cdot H_2O$, showing the vanadium octahedra (grey in the electronic version of the paper). The P, O and H atom types are indicated.

## Experimental

Both title compounds were prepared by hydrothermal treatment starting from mixtures of vanadium(V) oxide, caesium carbonate, oxalic acid, phosphoric acid and water. For the preparation of (I), a mixture of $V_2O_5$ (1 mmol), $H_2C_2O_4\cdot 2H_2O$ (2 mmol), $Cs_2CO_3$ (2 mmol), $H_3PO_4$ (17 mmol) and water (170 mmol) was loaded in a 23 ml-capacity Teflon-lined stainless steel Parr hydrothermal reaction vessel and heated at 393 K for 3 d. After slow cooling of the reaction vessel to room temperature, pale-green crystals were recovered by vacuum filtration, washed with water and dried in a desiccator.

For the preparation of (II), a mixture of $V_2O_5$ (1 mmol), $H_2C_2O_4\cdot 2H_2O$ (0.92 mmol), $Cs_2CO_3$ (2 mmol), $H_3PO_4$ (0.25 ml of an 85% solution) and water (4.75 ml) was loaded into a similar vessel as in the preparation of (I) and heated at 493 K for 72 h. The final product, a mixture of black and green crystals, was filtered off, rinsed with water and dried in a desiccator. Green crystals, corresponding to (II), were manually selected for single-crystal X-ray data collection. Attempts to obtain a pure phase remain unsuccessful.

### Compound (I)

*Crystal data*

$Cs_2V_2O_3(PO_4)(HPO_4)$
$M_r$ = 605.64
Monoclinic, $P2_1/c$
$a$ = 8.9180 (2) Å
$b$ = 16.9479 (4) Å
$c$ = 7.2199 (1) Å
$\beta$ = 99.092 (1)°
$V$ = 1077.52 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 8.74 mm$^{-1}$
$T$ = 293 K
0.16 × 0.15 × 0.15 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.251, $T_{max}$ = 0.277
18070 measured reflections
5051 independent reflections
4170 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.055
$S$ = 1.14
5051 reflections
154 parameters
H-atom parameters not defined
$\Delta\rho_{max}$ = 1.70 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.53 e Å$^{-3}$

### Compound (II)

*Crystal data*

$Cs_2[(VO)_3(HPO_4)_4(H_2O)]\cdot H_2O$
$M_r$ = 878.52
Monoclinic, $P2_1/c$
$a$ = 12.5465 (1) Å
$b$ = 11.9181 (1) Å
$c$ = 12.6531 (1) Å
$\beta$ = 96.7859 (6)°
$V$ = 1878.77 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 5.72 mm$^{-1}$
$T$ = 293 K
0.30 × 0.25 × 0.19 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.208, $T_{max}$ = 0.293
40158 measured reflections
12989 independent reflections
9367 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.095
$S$ = 1.02
12989 reflections
272 parameters
H-atom parameters not defined
$\Delta\rho_{max}$ = 3.64 e Å$^{-3}$
$\Delta\rho_{min}$ = −3.14 e Å$^{-3}$

In both title compounds, the H atoms on the hydrogenphosphate groups and the water molecules could not be located from difference Fourier maps. The largest electron-density peaks in the final difference Fourier syntheses are close to Cs atoms in both structures [at distances of 0.64 and 0.59 Å for compounds (I) and (II), respectively].

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg, 1998); data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3221). Services for accessing these data are described at the back of the journal.

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